MODEL MID TERM PAPER
GOVT. WOMEN ENGINEERING COLLEGE, AJMER

B.Tech. II Semester

Mid term Test **Engineering Chemistry**

Time : 1 hr. Max. Marks : 20

Attempt any four questions. First question is compulsory.

1. (a) What is hardness of water? 1
   (b) Write the name of two primary fuels. 1
   (c) Define carbonization. 1
   (d) Draw structure of Natural Rubber. 1
   (e) Define refractoriness. 1
2. Write short note on (any two) 5
   (i) Synthetic Petrol (ii) Zeolite Process
   (iii) Glass (iv) Caustic Embrittlement
3. Describe manufacturing of Portland cement by Rotary Kiln Technology. 5
4. Explain Thick film lubrication. 5
5. Explain electrochemical theory of corrosion 5

Answers

1. (a) What is hardness of water?

Ans. - Hardness is the property of water which prevents lather formation with soap. It is also called soap consuming property of water.

1. (b) Write the name of two primary fuels.

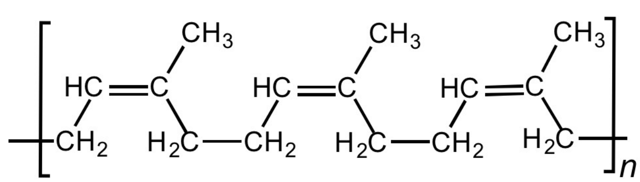
Ans. - (i) Coal (ii) Wood

1. (c) Define carbonization.

Ans. - It is the process of heating the coal in absence of air to a sufficiently high temperature so that the coal undergoes decomposition and yields the coke which is richer in carbon content than the original coal. So it is the process of converting the coal into coke.

1. (d) Draw structure of Natural Rubber.

Ans. Natural rubber is poly cis isoprene. It has following structure -



1.(e) Define refractoriness.

Ans. - Refractoriness is the ability of a material to withstand at high temperature without softening or deformation under working condition.

2. Write short note on (any two)

(i) Synthetic Petrol

The petrol synthesized by chemical methods is called synthetic petrol. Increase demand of petrol has necessity to synthesize petrol by chemical methods. The various methods for synthesis of petrol are - Polymerization, Alkylation, Fischer-Tropsch Process, Bergius Process

Polymerization - The gases obtained as a by-product from cracking of heavy oils contains lower olefins and alkanes. When this gaseous mixture is subjected to high pressure and temperature with or without the presence of catalyst, it get polymerizes to form higher hydrocarbons resembling gasoline.

$CH_3\text{-}CH{=}CH_2 + CH_3\text{-} CH_2\text{-}CH{=}CH_2 \longrightarrow CH_3\text{-} CH(CH_3)\text{-} CH_2\text{-}CH{=}CH_2$

Propene 1-Butene 5 Methyl 1-Haxene

Alkylation-

The process of alkylation i.e. the replacement of hydrogen by alkyl group is also used to obtain gasoline of better quality.

$CH_3\text{-}CH(CH_3)\text{-} CH_3 + CH_3\text{-}C(CH_3){=}CH_2 \longrightarrow CH_3\text{-}CH(CH_3)\text{-} CH_2\text{-} C(CH_3)_3$

Isobutane Isobutene Iso octane

Fischer-Tropsch Process -

In this process, mixture of pure water gas and hydrogen at ordinary pressure and at 200-300° C temperature in presence of catalyst gives a mixture of alkane and alkenes. A fraction resembling gasoline can be separated by fractional distillation.

$n\,CO + 2n\,H_2 \longrightarrow C_nH_{2n} + n\,H_2O$

Water gas Mixture of hydrocarbons

$n\,CO + (2n + 1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$

Bergius Process -

This process involves the conversion of low grade coals such as bituminous, into liquid and gaseous fuel by hydrogenating them in presence of catalyst. This method was developed by Bergius in Germany.

$n\,C + n\,H_2 \longrightarrow C_nH_{2n}$

Coal Mixture of hydrocarbons

$n\,C + 2n\,H_2 \longrightarrow C_nH_{2n+2}$

(ii) Zeolite Process

Permutit or Zeolite is a sodium-aluminium ortho silicate having formula$Na_2Al_2Si_2O_8.xH_2O$ or Na_2Ze where $Ze = Al_2Si_2O_8.xH_2O$. It occur naturally or can be manufactured synthetically. The use of Permutit as softener is based on the fact that it exchanges its sodium ions easily with the heavy metal ions (such as $Ca^{*\,2}$ and Mg^{*2}) present in hard water, e.g.

$Na_2Al_2Si_20_8 + CaCl_2 \longrightarrow CaAl_2Si_2O_8 + 2\,NaCl$

Process -

Zeolite softener consists of a steel tank packed with a thick layer of permutit. Hard water is percolated through the permutit when Ca and Mg salts present in it are removed in the form of insoluble zeolites and the resulting soft water is collected from the tap T.

Removal of Temporary and Permanent Hardness -

(i) $Ca(HCO_3)_2, + Na_2Ze \longrightarrow CaZe + 2\,NaHCO,$

(ii) $Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe$ •$+ 2\,NaHCO_3$

(iii) $CaCl_2 + NaZe \longrightarrow CaZe + 2\,NaCl$

(iv) $CaSO_4 + NaZe \longrightarrow CaZe + Na_2SO_4$

(v) $MgCl/MgSO_4 + NaZe \longrightarrow MgZe + NaCl/Na_2SO_4$

Thus, both temporary and permanent hardness can be removed by this method.

Regeneration of Permutit-

"Activation of exhausted permutit is called Regeneration."Permutit can work about 1 2 hours, after that, it is completely converted into Ca and Mg zeolites and it ceases to soften water. It can be made active (regeneration) again by passing 10% solution of NaCl.

$CaZe + 2\,NaCl \longrightarrow NaZe + CaCl_2$

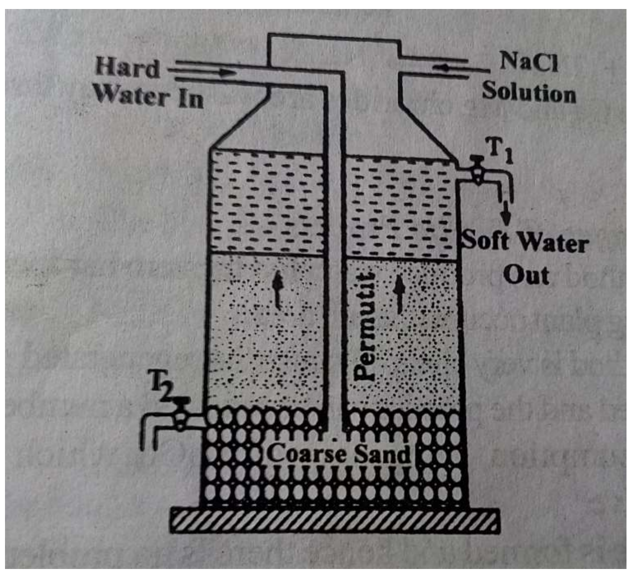
Exhausted Zeolite — Regenerated Permutit

$MgZe + 2NaCl \longrightarrow NaZe + MgCl_2$

Soluble Ca and Mg chlorides are washed away through tap.

Advantages of Zeolite Process -

1. This method can produce water having zero hardness.
2. Softening plant occupies small area.
3. This method is very cheap because the regenerated permutit is again used and the process can be repeated a number of times; the consumption being only of NaCl, which is almost inexpensive.
4. No sludge is formed and hence there is no problem of sludge disposal.
5. The process can be made automatic and continuous.
6. This process automatically adjusts itself for different hardness of incoming water.



(iii) Glass

"Glass is an amorphous, hard, brittle, transparent supercooled liquid with infinite viscosity." Chemically, glass is a mixture of silicates of sodium, potassium, calcium and lead. Within certain limits the glass may be represented by the general formula - $xR_2O.yMO.6SiO_2$, where,

R=Monovalent metals (Na, K)

M=Bivalent metals (Ca, Pb, Zn) and x and y are the whole numbers

Thus approximate composition of ordinary glass may be represented as $Na_2O.CaO.6SiO_2$ (soda-lime glass).

In some cases, in place of silica, oxides of aluminium, boron and phosphorus (Al_2O_3, B_2O_3, P_2O_5 etc.) are used.

PROPERTIES OF GLASS

Physical Properties -

1. It is transparent, amorphous, supercooled liquid.
2. It is hard, rigid, brittle and have no definite melting point.
3. It have high viscosity. (10^{13} poise)
4. They are insulators of heat and electricity.
5. It can incorporate coloring material, preserving transparency.

Chemical Properties -

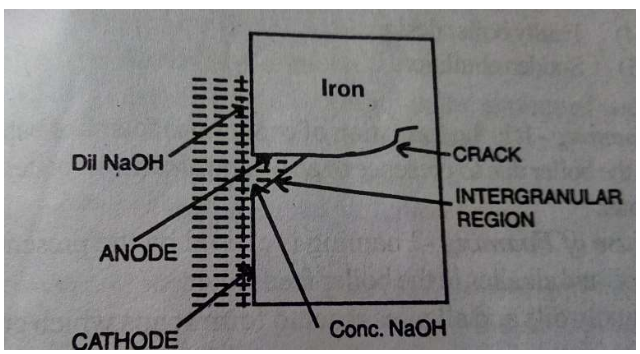
1. Glass is not attacked by air and oxidizing agents.
2. Ordinary glass is readily attacked by alkalis.
3. It has resistance towards acids except HF acid which dissolves the glass.

$Na_2O.SiO_2 + 6HF \longrightarrow 2NaF + SiF_4 + 3H_2O$

$CaO.SiO_2 + 6HF \longrightarrow CaF_2 + SiF_4 + 3H_2O$

(iv) Caustic Embrittlement

Caustic Embrittlement is the phenomenon during which boiler material becomes brittle due to the accumulation of caustic substances in boiler. Generally, it take place in high pressure boilers due to the presence of highly alkaline water.



Mechanism -

1. In water softening processes, Na_2CO_3 is added to boiler water to precipitate out Ca and Mg as their carbonates. But at high pressure and temperature, the residual Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide. Due to the formation of NaOH, the boiler water becomes alkaline.

$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$

Sodium Carbonate Sodium Hydroxide

2. When this slightly alkaline water flows into the minute hair-cracks or crevices, the water evaporates and hence concentration of caustic soda (NaOH) increases.

3. Now, at high temperatures in cracks and at joints under stress, this concentrated NaOH dissolves iron and form sodium ferroate.

$Fe + 2NaOH \longrightarrow Na_2FeO_2 + H_2$

Sodium Ferroate

4. At high operating temperatures, this sodium ferroate decomposes as -

$$3\ Na_2FeO_2 + 4\ H_2O \longrightarrow 6\ NaOH + Fe_3O_4 + H_2$$

Due to regeneration of NaOH, further dissolution of iron takes place.

Prevention of Caustic Embrittlement-

It can be prevented by -

Using sodium phosphate for water softening instead of sodium carbonate. Preventing the entry of NaOH into crevices by blocking them with innocuous harmless substances like -

(i) By adding tannin or lignin as additive to the boiler water.

(ii) By adding sodium sulphate to the boiler water.

3. Describe manufacturing of Portland cement by Rotary Kiln Technology.

Ans - *Raw materials required* - The major raw materials used for the manufacturing of Portland Cement are -

1. **Calcareous Materials -** These are the $CaCO_3$ containing compounds like lime stone, e.g.- Chock, Marble etc.

2. **Argillaceous Materials -** It includes mainly silicate containing compounds, e.g.- Clay, Shale, Slate, Blast Furnace, Slag etc.

3. **Additive -** These are the compounds which are used to improve the quality of cement, e.g.- Gypsum ($CaS0_4.2H_2O$)

Manufacturing Process -

Manufacturing of Portland Cement by Rotary Kiln Technology involves following three steps -

(i) Preparation of the raw mixture (Mixing)

(ii) Production of the clinker (Burning)

(iii) Preparation of the cement (Grinding).

(i) Mixing (Mixing the raw materials) - Mixing of raw materials can be done either by - Dry Process or by Wet Process.

Dry Process - This process is adopted where hard clay such as shale and lime stone cement rock are generally used. In this process, the raw materials are separately crushed and grounded then mixed.

Wet Process - This process is adopted when raw materials don't have any inherent moisture content of 15% or more because it is uneconomical to drive away the excessive quantity of water. In this method powdered raw materials are mixed and then water is added to form slurry of raw materials.

(ii) Burning (Burning the mixture in Rotary Kiln) **- In a** rotary kiln, ground mixture is burnt to form clinker. Rotary Kiln consists of a long steel cylinder, lined with refractory bricks and rotating at a speed of 0.5 to 2 rotation/min. The kiln is slightly inclined at a angle of 3°-6°C. The inclination allows the material fed in the upper end to travel slowly to the other end. The kiln is mounted on the roller bearings. The raw materials are fed from the upper end of the rotary kiln and the burning fuel (Pulverized Coal) and air are injected at the lower end, heat up the kiln to a temperature of about 1500°-1600°C.

The chemical reactions which takes place in the kiln are divided into the following zones -

(a) Drying Zone - This is the upper part of the kiln. In this zone moisture and slurry gets evaporated. The dry material passes down the kiln.

(b) Calcination Zone - This is the central part of the kiln, where the temperature is about 900°-1000° C. The dry material reaching in this part undergoes decomposition of lime stone to form CaO and CO_2.

$$\mathbf{CaCO3 \longrightarrow CaO + CO_2}$$

CO_2 escapes out and material acquire the shape of lumps.

(c) Burning of Clinkering Zone - This is the hottest zone of the kiln having a temperature of about 1400°-1500°C. Here the main reaction between the lime and clay takes place resulting in the formation of aluminates and silicates of calcium.

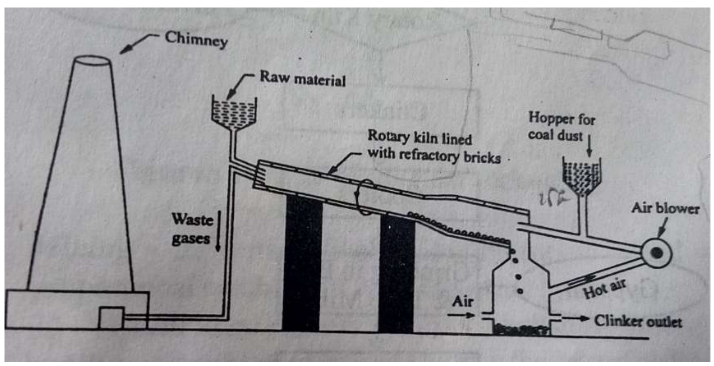
$2\,CaO + SiO_2 \longrightarrow Ca_2SiO_3$

$3\,CaO + SiO_2 \longrightarrow Ca_3SiO_5$

$3\,CaO + A1_2O_3 \longrightarrow Ca_3Al_20_6$

These calcium aluminates and silicates combine together to form small hard grayish stones called *Clinkers.* The clinker falls out from the lower end of the kiln into coolers where it is cooled by the atmospheric air. The air thus becomes hot and is used for blowing the fuel placed at the lower end.

(d) Grinding - The cooled clinkers are ground to fine powder by ball mills. During final grinding 2-5% of gypsum is added to retard or delay the setting of cement when it comes in contact with water.



4. Explain Thick film lubrication.

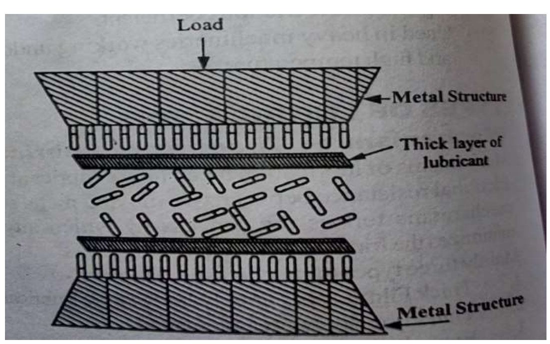
Ans. - In such type of lubrication, the lubricant is used in sufficient quantity so that the lubricated surfaces are separated completely by a thick film of lubricant (Have at least 1000 A° thickness).

This type of mechanism applied when -

(i) The load applied on machine is not too high.

(ii) Generally, it is applied when one of the rubbing surfaces is slightly displaced in relation to the other.

(iii) This type of mechanism is mainly suitable for delicate instruments (Light machines) e.g.- watches, clocks, guns, scientific instruments, sewing machines.



Mechanism- The thick film covers (fills) all the irregularities of both the metal surfaces. In this mechanism, the thick layer of lubricant totally avoid the direct contact between two moving metal surfaces. In such type of lubrication, the resistance to motion is only due to the internal resistance between the particles of the lubricant. In this type of lubrication, to minimize this internal resistance, the lubricant chosen should have enough viscosity to provide good lubrication. For such system, the friction coefficient is as low as 0.001 to 0.003. Hydrocarbon oils are most suitable lubricating oils for thick film lubrication. The best example for illustration of hydrodynamic lubrication is journal (shaft) bearing.

5. Explain electrochemical theory of corrosion.

Ans. Electrochemical theory is the most widely accepted theory for the explanation of wet corrosion. This type of corrosion takes place under the two following conditions -

(a) When the metal surface is in contact with the conducting liquid

(b) When two different metal are in contact with each other and partially or completely immersed in a solution.

According to electrochemical theory, chemically the non- uniform surfaces of metal behaves like small electric cell in presence of aqueous medium. Hence corrosion in presence of water is an electrochemical phenomenon which involves - (i) The formation of cathodic and anodic areas which are in

(ii) Flow of electric current between cathodic and anodic areas.

(iii) Formation of corrosion product somewhere between the cathodic and anodic areas.

Anodic reaction -

Oxidation $M \longrightarrow M^{n+} + n\,e^-$

M^{n+} dissolves in solution and forms metal oxide The anodic reaction involves dissolution of metal as metal ions with the liberation of electrons.

In *cathodic reaction,* electrons are consumed, which are evolved in anodic reaction. Besides the consumption of electrons, (i) evolution of *hydrogen* or (ii) absorption of O_2 also takes place. This depends upon the corrosive environment.

Evolution of H_2-

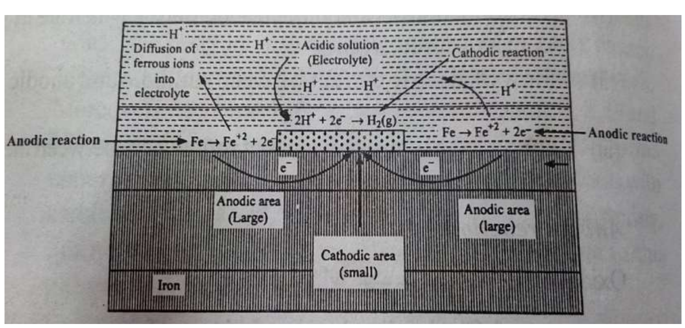
This type of corrosion takes place in acidic environment, e.g. - Corrosion of Fe.

(a) Anodic reaction -

In acidic medium, the anodic reaction involves the dissolution of Fe as Fe^{+2}ion with the liberation of electrons.

$Fe \longrightarrow Fe^{+2} + 2\,e^-$

These electrons flow from anode to cathode through the metal.



(b) **Cathode reaction -**

At cathodic area the H^+ ions obtained from acids solution get reduced and H_2 gas is evolved.

$2H^+ + 2e- \longrightarrow H_2O$

Overall reaction -

$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$

Absorption of oxygen -

Rusting of iron in presence of neutral aqueous solution is the most common example of this type of corrosion.

In presence of atmospheric oxygen, iron surface is coated with thin film of iron oxide but if this film develops some cracks, then it causes anodic areas on the surface while except this part, remaining portion acts as cathode.

Anodic Reaction -

At anodic area; $Fe \longrightarrow Fe^{+2} + 2e-$

oxidation takes place. These electrons flow from anodic area to cathodic area.

Cathodic Reaction -

At cathodic area; the dissolved oxygen present at cathodic area gets reduced by taking up electrons which comes from the anodic area.

$\mathbf{1/2\ O_2 + 2e- + H_2O \longrightarrow 2OH^-}$

Now both ions Fe+^{2} and OH" diffuses and combine to form Iron Hydroxide [$Fe(OH)_2$].

$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2$

Ferrous Hydroxide

If enough oxygen is present -

$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$ or $Fe_2O_3.H_2O$

(Yellow Rust)

If limited amount of oxygen is present; the corrosion product may be black anhydrous magnetite Fe_3O_4.